

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 May 2003 (22.05.2003)

PCT

(10) International Publication Number
WO 03/042333 A1

(51) International Patent Classification⁷: **C10G 49/00**

(21) International Application Number: PCT/EP02/12856

(22) International Filing Date:
15 November 2002 (15.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01309668.0 16 November 2001 (16.11.2001) EP

(71) Applicant (for all designated States except US): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ROOVERS, Anto-
nius, Adrianus, Maria** [NL/NL]; Badhuisweg 3, NL-1031
CM Amsterdam (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

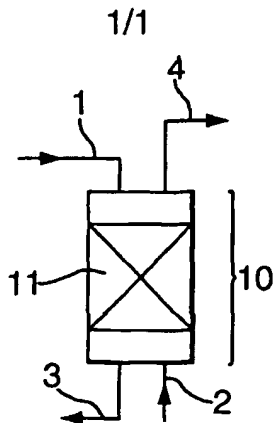
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **COUNTERCURRENT HYDROPROCESSING**



(57) Abstract: Method for the hydroprocessing of a heavy hydrocarbonaceous feedstock in a reaction zone (10) comprising a bed (11) containing a fixed array of porous catalyst particles by contacting the feedstock with a hydrogen-containing gas under conditions which allow distributing the feedstock predominantly in liquid phase under superatmospheric process conditions at elevated temperature over the catalyst bed (11) for downward flow in contact with the catalyst particles and introduction of the hydrogen-containing gas in the reaction zone (10) below the catalyst bed (11) in order to establish countercurrent contact of the upwardly flowing gas with the downcoming liquid and withdrawing treated liquid below the catalyst bed (11) and withdrawing fluid depleted in hydrogen above the catalyst bed (11), in which process the catalyst bed (11) has a void volume fraction below 0.5, whilst the countercurrent liquid/gas contacting is carried out under conditions which allow the Peclet number of the liquid to be in the range between 0 and 10.

WO 03/042333 A1

COUNTERCURRENT HYDROPROCESSING

The present invention is concerned with a method for hydroprocessing a hydrocarbonaceous feedstock at elevated temperature and pressure to obtain products, in particular fuels and/or middle distillates, which can be
5 obtained in rather high yields at relatively low hydrogen consumption.

Hydroprocessing is well known in the art and has been practiced for many years and is still one of the important refinery processes. Over the years, a variety
10 of feedstocks, catalysts and process conditions have been described for hydroprocessing of which many have been put into practice. For instance, in hydrocracking it is customary to pass the feedstock to be hydrocracked together with a hydrogen-containing gas over a catalyst
15 bed containing a fixed array of particles containing one or more metal compounds having an intrinsic capability for breaking carbon-carbon bonds as well as one or more metal compounds having an intrinsic capability of hydrogenating fragments present after the cracking
20 operation has been performed.

The method of hydrocracking in which a feedstock and a hydrogen-containing gas are passed through the catalyst bed in the same direction, normally from top to bottom to make use of the gravity force, is known as co-current
25 hydroprocessing. It is the oldest commercially applied hydrocracking method which is still in operation.

In the early 70's it has been suggested to operate hydrotreating processes in so-called "split flow" mode. In such processes, described inter alia in US 3,607,723,
30 US 3,671,420 and US 3,897,329, the feedstock is invariably introduced between two catalyst beds in a

reaction zone whilst hydrogen is introduced from the bottom of the catalyst bed over which the feedstock is being distributed to be passed downwardly through the catalyst bed. In essence, the process carried out in the downstream bed (seen from the point of entry of the feedstock) is operated in countercurrent mode (feedstock moving downward meeting uprising hydrogen) whilst the process carried out in the catalyst bed above the catalyst bed over which the feedstock is being distributed is carried out in cocurrent mode (uprising hydrogen and fluid stripped by the uprising hydrogen moving in the same direction). In such "split flow" processes, use has to be made of two reaction zones which are preferably operated under the same process conditions.

Although it was recognised that operating in countercurrent mode may provide some alleviation of flow maldistribution of the mixed phase present in cocurrent flow, there is nevertheless a major constraint which severely affects countercurrent hydroprocessing.

A major constraint in countercurrent hydroprocessing is the risk that conventional fixed bed reactors are susceptible to a phenomenon normally referred to as "catalyst bed flooding" which will occur when the velocity of the upflowing hydrogen-containing gas is such that it prevents the downward gravitational flow of the feedstock to be hydroprocessed during its passage through the catalyst bed. Although catalyst contacting might improve as the bed approaches a flooded condition, it also makes the process rather vulnerable towards fluctuations in pressure or temperature or in fluid flow rates. Should a disturbance occur which is capable of initiating flooding it would cause disruption of the process, even to the extent of an unscheduled shutdown in order to recover stable operation.

In order to minimise the occurrence of flooding in reactors operating in countercurrent mode it has been proposed, inter alia in patent publication WO 99/00181, to provide the hydroprocessing reactor with gas bypass means which are self-regulating and which allow carrying out the operation closer to the flooding point of the reactor. However, additional equipment has to be installed and the threat of flooding still occurring has not been taken away completely.

It has been described in US 4,775,281, which is directed at the treatment of heavy hydrocarbons in countercurrent mode with specific froth control, that achievement of uniform vertical flow through a porous bed of solids can be obtained if the catalyst is properly distributed and shaped. The teaching of US 4,775,281 is specifically that the use of a densely packed bed of (spherical) solids (causing the reaction zone to have a low void fraction) would be advantageous in terms of catalyst concentration, but there might well be interference with fluid flow, especially when countercurrentflow of two phases is required. Therefore, it is strongly recommended in said patent specification that the catalyst bed to be used has a high void volume, typically greater than one-half of the bed. By using loosely packed polylobal or cylindrical extrudates void fractions from 0.5 to 0.9 can be achieved. This means a large sacrifice with respect to available reactor volume (at least half of the reactor volume cannot be filled with catalyst particles) which tremendously affects the yield of the envisaged process.

It has now been found that countercurrent hydroprocessing can be carried out in reaction zones having a lower void fraction and which do not require specific means for preventing flooding of the catalyst bed. The countercurrent hydroprocessing method according to the

present invention is preferably carried out under flooding conditions. It also allows a higher yield than is achievable in cocurrent hydroprocessing. It has also been found that the process in accordance with the present invention allows a lower consumption of expensive hydrogen, a higher heavy ends conversion and a higher selectivity in the sulphur removal of higher boiling sulphur containing components.

The present invention therefore relates to a method for the hydroprocessing of a heavy hydrocarbonaceous feedstock in a reaction zone comprising a bed containing a fixed array of porous catalyst particles by contacting the feedstock with a hydrogen-containing gas under conditions which allow distributing the feedstock predominantly in liquid phase under superatmospheric process conditions at elevated temperature over the catalyst bed for downward flow in contact with the catalyst particles and introduction of the hydrogen-containing gas in the reaction zone below the catalyst bed in order to establish countercurrent contact of the upwardly flowing gas with the downcoming liquid and withdrawing treated liquid below the catalyst bed and withdrawing fluid depleted in hydrogen above the catalyst bed, in which process the catalyst bed has a void volume fraction below 0.5, whilst the countercurrent liquid/gas contacting is carried out under conditions which allow the Peclet number of the liquid to be in the range between 0 and 10.

Without wishing to be bound to any particular theory, it would appear that operating in a gas/liquid regime characterised by a low Peclet number of the liquid (i.e. by allowing a certain amount of liquid backmixing) allows the use of relatively dense-packed catalyst particles which therefore substantially increases the yield of the desired products. In other words: by providing process

conditions which reduce the amount of static liquid hold up and thereby increase the amount of dynamic liquid hold up, unwanted reactions are diminished and more middle distillates are produced than otherwise would be the case. The combination of using a lower void fraction of the catalyst and a reduced ratio of the static and dynamic hold up of the liquid phase allows for improved performance in countercurrent hydroprocessing.

Parameters which can be instrumental in providing countercurrent liquid/gas contacting comprise, inter alia, the gas rate (an increased gas rate reducing the unwanted static hold up), the liquid flow and the size of the restrictions in the introduction means for the gas. Those skilled in the art will know how to apply one or more of such parameters to allow for the appropriate Peclet number to be reached in the countercurrent hydroprocessing method according to the present invention.

The void volume fraction of a catalyst bed is defined for the purposes of this invention as 'one minus the fraction of the volume occupied by the catalyst particles of the total volume of the reaction zone'. It will be clear that the internal pore volume of the solid catalyst particles is not included in the definition of the void volume fraction which is built up of the interstitial voids between the catalyst particles and between the appropriate catalyst particles and the walls of the reaction zone in which they are contained.

Suitably, void volume fractions of catalyst beds above 0.25 (and below 0.50) can be used in the method according to the present invention. Preferred values are in the range between 0.30 and 0.48, especially preferred values are in the range between 0.35 and 0.47. Impressive results have been obtained using catalyst particles which have been packed in such a way that the void volume

fraction is 0.45 (whilst operating under conditions allowing for the Peclet number of the liquid to be between 0 and 10).

5 The Peclet number for systems in which liquids and gases come into contact with each other whilst the solid phase is fixed, as is the case in hydroprocessing using fixed arrays of porous solid catalyst particles, can be defined as the ratio between the transport rate by convection and the transport rate by dispersion; Chemical
10 Reactor Design and Operation. K. Westerterp et. al. ISBN 0 471 90183 0. The Peclet number for a totally back-mixed system (normally occurring when operating under CSTR conditions - CSTR meaning Continuously Stirred Tank Reactor) is defined as 0 whilst the Peclet number of a
15 system operating in plug flow (e.g. in conventional trickle flow hydrocracking) in which by definition back-flow is absent is defined as infinite (∞). The preferred range for the Peclet number of the liquid in the method of the present invention is between 1 and 8. It will be
20 clear to those skilled in the art how to calculate the actual Peclet number for a given situation. As stated hereinbefore, it is the combination of the use of a catalyst bed having a low void fraction under conditions which allow a low Peclet number of the liquid which allow
25 for the improved performance of the hydroprocessing method according to the present invention.

The catalysts to be used in the hydroprocessing method according to the present invention are well known in the art. They normally contain one or more metal(s) of
30 Group VI and/or one or more non-noble metal(s) of Group VIII of the Periodic Table of the Elements which are conveniently present as oxides and/or as sulphides. Suitable Group VI elements are molybdenum and tungsten; suitable Group VIII metals are nickel and cobalt. The
35 amounts of the metal compound(s) to be used can vary

between wide ranges. Suitable ranges are between 2 and 40% by weight of Group VI metal compounds, expressed as metal, and between 1 and 10% by weight of Group VIII metal compounds, expressed as metal.

5 Normally the catalyst particles will have the catalytically active metals present on a carrier. Suitable carrier materials are inorganic refractory oxides such as alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures of two or more of such
10 materials. Advantageously, the catalyst particles may (additionally) contain dedicated cracking components such as zeolites and/or amorphous silica-alumina. Examples of suitable cracking components are well known in the art. Suitable zeolites comprise zeolite Y and zeolite β but
15 also non-zeolitic components can be used such as (silico)-alumino phosphates and related compounds.

A wide variety of catalyst shapes can be used in the method of hydroprocessing according to the present invention, such as spherical particles, cylindrical
20 particles and polylobal particles such as trilobes and quadrulobes. Good results have been obtained using trilobal catalyst particles. Particles having a largest diameter between 0.5 and 3.5 mm are preferably applied. Good results have been obtained using trilobal catalyst
25 particles having a diameter of 1.6 mm.

The hydroprocessing method according to the present invention can be conveniently carried out using a temperature in the range between 200 °C and 475 °C, preferably in the range between 250 °C and 425 °C and at
30 a pressure between 20 and 250 bar, preferably between 40 and 160 bar. The process can be carried out at a LHSV in the range between 1 and 20 Nl feed/l catalyst/hr and at a hydrogen/hydrocarbon feed ratio in the range between 100 and 2000 Nl/l, preferably between 250 and 1500 Nl/l. It
35 will be clear that the set of process conditions has to

be chosen in such a way that it allows the Peclet number of the liquid to be in the range between 0 and 10 (the void volume fraction of the catalyst bed in the reaction zone being less than 0.5 as discussed hereinbefore).

5 Heavy hydrocarbonaceous feedstocks to be used in the method according to the present invention comprise the usual feedstocks which are commercially used in hydrocracking such as heavy gas oils and the like. Suitable feedstocks have an initial boiling point of at
10 least 200 °C whilst feedstocks containing substantial amounts of material boiling above 520 °C, e.g. containing up to 40% by weight of such material, can also be processed satisfactorily.

 Commercially available hydrogen can be suitably used
15 in the method according to the present invention. It may contain indigenous impurities to an extent that they do not substantially affect the catalytic activity. Hydrogen streams containing at least 50% by volume of hydrogen, especially at least 80% by volume, are preferred for duty
20 in the present method. Normal impurities comprise light hydrocarbons and nitrogen.

 There are a number of process configurations which can be used advantageously in the method according to the present invention. Five line-ups of particular interest
25 are described hereinbelow but those skilled in the art will recognise that equivalent line-ups can also be used. In Figure 1 the basic line-up is described for counter-current hydroprocessing. A first and second preferred line-up are described in Figures 2A and 2B, a third
30 preferred line-up is described in Figure 3 and a fourth preferred line-up is described in Figure 4. The same numerals have been used for the same parts in each of the Figures.

Figure 1 (basic line-up)

Liquid feedstock is introduced via line 1 at the top of reaction zone 10 containing catalyst bed 11 and is distributed (means not shown) over the catalyst bed whilst a hydrogen-containing gas is introduced via line 2 below catalyst bed 11 in reaction zone 10 and rises up through the catalyst bed. Treated liquid is withdrawn from reaction zone 10 via line 3 and can be used as such or may be subjected to further processing/upgrading (not shown) and fluid depleted in hydrogen is withdrawn from reaction zone 10 via line 4 which can be cooled down in order to separate off liquid present therein (means not shown). The process as described in Figure 1 is carried out under conditions which allow a low Peclet number for the liquid in catalyst bed 11.

Figure 2A (further treatment of treated liquid)

The line-up as described in Figure 1 is extended by the presence of a further reaction zone 20 containing catalyst bed 21 downstream of catalyst bed 11 which catalyst bed 21 allows operation under trickle flow conditions (i.e. under conditions generating a high Peclet number for the liquid phase). Treated liquid emanating from the bottom of reaction zone 10 is passed through catalyst bed 21 in reaction zone 20 and withdrawn there from via line 5. It can be used as such or be subjected to further treatment (not shown). In this line-up there is no separate inlet for a hydrogen-containing gas (but it may be present if desired).

Figure 2B (further treatment of both treated liquid and fluid depleted in hydrogen)

The line-up as described in Figure 2B is that as described in Figure 2A with the addition of a further reaction zone 30 containing catalyst bed 31 above reaction zone 10 containing catalyst bed 11. Catalyst bed 31 is operated in trickle flow mode (high Peclet

number of the liquid) and fluid depleted in hydrogen is withdrawn via line 7 which can be cooled down in order to separate off liquid present therein (means not shown).

Optionally, liquid feedstock can be introduced

5 additionally via line 8 on top of catalyst bed 31 in reaction zone 30.

Figure 3 (three catalyst beds of which two are operated counter currently)

10 The line-up as described in Figure 2B is changed to the extent that the hydrogen-containing fluid is not introduced via line 2 but via line 12 at the bottom of reaction zone 20 containing catalyst bed 21. This line-up enables the process to be carried out in countercurrent mode with respect to catalyst beds 21 and 11 whilst
15 catalyst bed 31 is operated in trickle flow mode. It is possible to operate bed 21 and/or bed 11 under flooded conditions.

Figure 4 (combined further processing)

20 Liquid feedstock is introduced via line 1 at the top of reaction zone 10 containing catalyst bed 11 and is distributed (means not shown) over the catalyst bed whilst a hydrogen-containing gas is introduced via line 2 below catalyst bed 11 in reaction zone 10 and rises up through catalyst bed 11. Treated liquid is withdrawn from
25 reaction zone 10 and sent (at least partially) via line 3 to be combined with fluid depleted in hydrogen which has been (at least partially) withdrawn from reaction zone 10 via line 4. It is, of course, possible and preferred in practice, to allow part of the fluid exiting reaction
30 zone 10 via line 4 to be condensed so that a gas/liquid mixture will be combined with treated fluid ex line 3 to form feedstock entering reaction zone 40 via line 13. The mixture is thus sent via line 13 to reaction zone 40 containing catalyst bed 41 which is operated (as
35 hydroprocessing unit) in trickle flow mode (high Peclet

number of the liquid). The hydrogen required for this part of the process can be supplied via line 14 at the top of reaction zone 40, thereby allowing for cocurrent hydroprocessing of the mixture entering reaction zone 40 via line 13, or via line 14 at the bottom of reaction zone 40 thereby causing the catalyst bed 41 to be operated in countercurrent mode. Treated liquid is withdrawn via line 15 and fluid depleted in hydrogen is withdrawn via line 16.

The method according to the present invention will now be elucidated by the following, non-limiting Examples.

Example 1

In a cylindrical reactor (lay out as depicted in Figure 1) having a length of 65 cm and an internal diameter of 2 cm and containing 1.6 mm trilobal catalyst particles (composed of 20 %wt of ultra stable zeolite Y and 80 %wt of alumina-based silica-alumina containing 4 %wt of Ni and 17 %wt of W as hydrogenation components) a heavy gas oil was led downwardly through the catalyst bed and hydrogen was led via the bottom part of the catalyst bed in countercurrent to the heavy gas oil. The catalyst bed was loaded in such a way that the void fraction was 0.45. The Initial Boiling Point (IBP) of the gas oil was 230 °C; 62% boiled above 340 °C and its Final Boiling Point (FBP) was 450 °C. It contained 2.1 %wt of sulphur and 317 ppm of nitrogen.

Two experiments were carried out which differed only in the hydrogen gas rate applied. The details of experiments 1 and 2 are given in Table I below.

Table I

		Experiment 1	Experiment 2
Space velocity	Kg/l/h	0.75	0.75
H ₂ gas rate	Nl/h	250	1000
Reactor pressure	barg	40	40
Bed temperature	°C	390	390
Peclet number of the liquid		plug flow (*)	6
Conversion of 340 °C+	%	28.6	45.0
Selectivity to 150-340 °C	%	86.0	92.1

*) Under the conditions as pertaining in experiment 1 the process was carried out in a conventional trickle flow mode which is normally referred to as "plug flow" (see: Advantages, Possibilities and Limitations of Small Scale Testing of Catalysts for Fixed-Bed Processes: S.T. Sie, 210th National Meeting, American Chemical Society, Chicago, Ill., August 20-25, 1995, p 463-472). A Peclet number of the liquid of 16 emanates from this set-up.

The conditions as pertaining in experiment 2 can be described as flooded countercurrent yielding a Peclet number of the liquid of 6 (calculated using the Westerterp reference referred to hereinabove).

It can be seen that under conditions which allow a low Peclet number (in accordance with the present invention) not only the conversion of the 340 °C+ part of the feedstock (i.e. the fraction of the feedstock boiling between 340 °C and 450 °C) has been increased substantially (by almost 50%) but that at the same time also the selectivity to desired product has increased from 86.0% to 92.1%.

Example 2

The experiments as described in Example 1 were repeated at a different space velocity under otherwise directly comparable conditions. The details of experiments 3 and 4 are given in Table II.

Table II

		Experiment 3	Experiment 4
Space velocity	Kg/l/h	1.25	1.25
H ₂ gas rate	Nl/h	250	1000
Reactor pressure	barg	40	40
Bed temperature	°C	390	390
Peclet number of the liquid		plug flow (*)	2
Conversion of 340 °C+	%	19.3	37.0
Selectivity to 150-340 °C	%	94.9	95.9

*) see the comments under Table I.

It can be seen that the same trend is found when operating at a higher space velocity; in particular it should be noted that the conversion can be doubled whilst still gaining in selectivity to the desired product.

C L A I M S

1. Method for the hydroprocessing of a heavy hydrocarbonaceous feedstock in a reaction zone comprising a bed containing a fixed array of porous catalyst particles by contacting the feedstock with a hydrogen-
5 containing gas under conditions which allow distributing the feedstock predominantly in liquid phase under super-atmospheric process conditions at elevated temperature over the catalyst bed for downward flow in contact with the catalyst particles and introduction of the hydrogen-
10 containing gas in the reaction zone below the catalyst bed in order to establish countercurrent contact of the upwardly flowing gas with the downcoming liquid and withdrawing treated liquid below the catalyst bed and withdrawing fluid depleted in hydrogen above the catalyst
15 bed, in which process the catalyst bed has a void volume fraction below 0.5, whilst the countercurrent liquid/gas contacting is carried out under conditions which allow the Peclet number of the liquid to be in the range between 0 and 10.
- 20 2. Method according to claim 1, in which the catalyst bed has a void volume fraction above 0.25.
3. Method according to claim 2, in which the catalyst bed has a void volume fraction between 0.30 and 0.48, preferably between 0.35 and 0.47.
- 25 4. Method according to any one of the preceding claims, in which the countercurrent contacting is carried out under conditions which allow the Peclet number of the liquid to be in the range between 1 and 8.
5. Method according to any one of the preceding claims,
30 in which treated liquid which has passed downwardly

through a further bed containing catalytic particles prior to its withdrawal from the process and/or fluid depleted in hydrogen which has passed upwardly through the catalyst bed is passed upwardly in vapour phase
5 through a further bed containing catalytic particles prior to its withdrawal from the process as fluid depleted in hydrogen.

6. Method according to claim 5, in which at least part of the upwardly flowing hydrogen-containing gas is
10 introduced in the bottom of the reaction zone containing a further bed containing catalytic particles through which treated liquid is passed prior to its withdrawal from the process.

7. Method according to any one of claims 1 to 5, in
15 which at least part of the treated liquid and at least part of the fluid depleted in hydrogen are combined and subjected to a second hydroprocessing step which is carried out either cocurrently or counter currently.

8. Method according to any one of the preceding claims,
20 in which the hydroprocessing is carried out under hydrocracking conditions, including a temperature in the range between 200 °C and 475 °C and a pressure between 20 and 250 bar.

9. Method according to claim 8, in which catalyst
25 particles are used having a spherical, cylindrical or polylobal form and a largest diameter between 0.5 and 3.5 mm.

Fig.1.

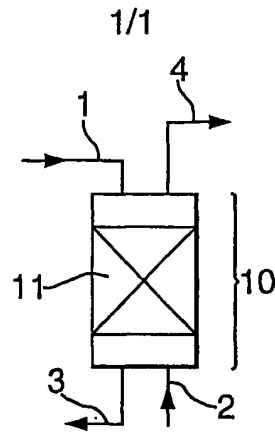


Fig.2A.

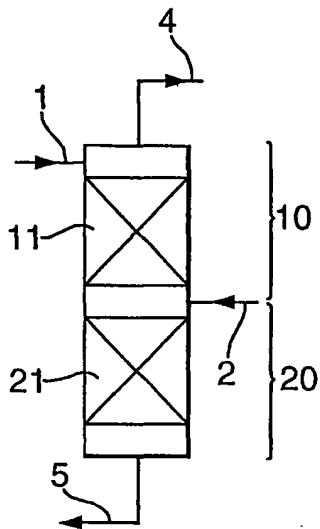


Fig.2B.

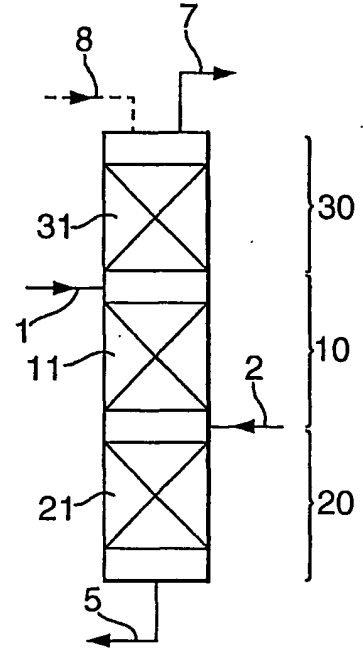


Fig.3.

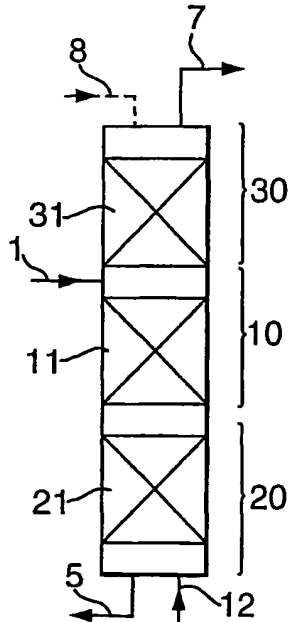
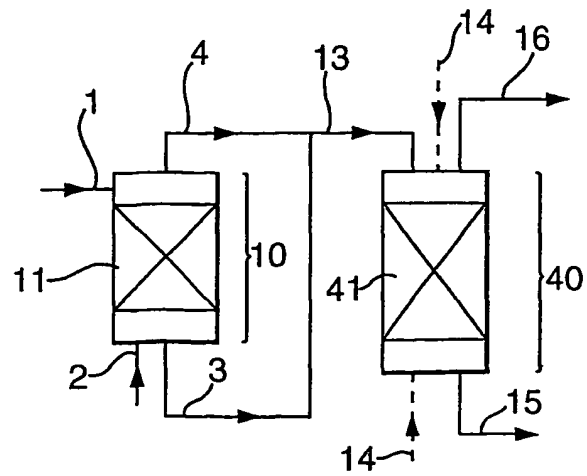


Fig.4.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12856

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G49/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 287 234 A (MOBIL OIL CORP) 19 October 1988 (1988-10-19) page 4, line 25 - line 34 page 3, line 54 - line 55; claims 1,4,5; figure 1 page 5, line 28 - line 31	1-5,8,9
Y	WO 01 72408 A (INST FRANCAIS DU PETROL ;GALTIER PIERRE (FR); HUGUES FRANCOIS (FR)) 4 October 2001 (2001-10-04) page 9, line 26 -page 10, line 11	1-5,8,9
A	US 5 578 197 A (CYR THEODORE ET AL) 26 November 1996 (1996-11-26) example 15	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 January 2003

Date of mailing of the international search report

29/01/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Deurinck, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/12856

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0287234	A	19-10-1988	AU 1408088 A	20-10-1988
			EP 0287234 A1	19-10-1988
			JP 1009289 A	12-01-1989
WO 0172408	A	04-10-2001	FR 2806642 A1	28-09-2001
			AU 3752201 A	08-10-2001
			EP 1268048 A1	02-01-2003
			WO 0172408 A1	04-10-2001
			NO 20024609 A	26-09-2002
US 5578197	A	26-11-1996	EP 0396384 A2	07-11-1990